

**PCT**WORLD INTELLECTUAL PROPERTY  
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER

WO 9608537A1

(51) International Patent Classification <sup>6</sup> :

C09B 67/20

A1

(11) International Publication Number:

WO 96/08537

(43) International Publication Date:

21 March 1996 (21.03.96)

(21) International Application Number: PCT/EP95/03462

(22) International Filing Date: 2 September 1995 (02.09.95)

(30) Priority Data:

9418499.1

14 September 1994 (14.09.94) GB

(71) Applicant (for all designated States except US): CIBA-GEIGY AG [CH/CH]; Klybeckstrasse 141, CH-4002 Basle (CH).

(72) Inventors; and

(75) Inventors/Applicants (for US only): ZAMBOUNIS, John [GR/CH]; Engelhardstrasse 41, CH-3280 Murten (CH). BIZE, ALine [CH/CH]; La Clamogne 62, CH-1633 Marsens (CH).

(74) Common Representative: CIBA-GEIGY AG; Patentabteilung, Klybeckstrasse 141, CH-4002 Basle (CH).

(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).

**Published***With international search report.**Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(54) Title: PROCESS FOR PRODUCING N-METHYLATED ORGANIC PIGMENTS

## (57) Abstract

A process for producing an organic pigment represented by the general formula (I):  $A(H)_x(CH_3)_y$ , characterized in that an organic pigment represented by the formula (II):  $A(H)_{x+y}$ , is reacted with dimethylcarbonate in the presence of a base with or without a solvent, wherein in formulae (I and II)  $x + y$  is an integer 1 to 4 with  $x$  being 0 to 4 and  $y$  being 1 to 4,  $A$  is the residue of an organic pigment containing  $x + y$  cyclic or open -NH- groups, and the H as well as  $CH_3$  in formula (I and II) are bound to the above mentioned N. This process is suitable for the production of N-methylated organic pigments in an environmentally safe process and at a low production cost.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

### Process for producing N-methylated organic pigments

The present invention relates to a process for the production of N-methylated organic pigments.

Some N-methylated organic pigments are known in the art. For example, N,N'-dimethyl-substituted pyrrolo[3,4-c]pyrroles are described in US Patent 4,585,878; N,N'-dimethyl-quinacridone is reported by L. L. Pushkina et al in Zh. Org. Khim. 20, 1939(1984); N,N'-dimethyl-substituted perylenedicarboxylic acid diimide is disclosed in US Patent 3,673,192; N,N'-dimethyl-indigo is described by G. A. Russel et al in J. Am. Chem. Soc., 91, 3851(1969).

These compounds are used especially as coloring agents for polymeric materials. The processes for the production of these compounds involve without exception the N-methylation step using methyl iodide or dimethyl sulfate as methylating agents.

However, the above mentioned methylating agents are of high toxicity, so that particular care must be exercised during the N-methylation process. Moreover, methyl iodide and dimethyl sulfate are expensive reagents. Accordingly, the prior art method for the N-methylation of organic pigments has drawbacks in that it can cause problems with respect to environmental protection and that the production cost of the N-methylated organic pigments are high.

It is therefore desirable that an alternative process be developed which is environmentally safe and which enables the production of N-methylated organic pigments at a low production cost.

On the other hand, it is described in M. Lissel et al, Synthesis, 382, (1986) that imidazole can be methylated in good yield by using dimethyl carbonate under phase transfer conditions.

However, M. Lissel et al neither disclose nor suggest that insoluble organic pigments can,

- 2 -

surprisingly, be N-methylated in suspensions in good yield by using dimethyl carbonate and a base but without using a phase transfer catalysts, thereby enabling the production of N-methylated organic pigments at a low production cost in an environmentally safe process.

Accordingly, the present invention relates to a process for producing an organic pigment represented by general formula



characterized in that an organic pigment represented by formula



is reacted with dimethylcarbonate in the presence of a base with or without a solvent, wherein in formulae I and II  $x + y$  is an integer 1 to 4 with  $x$  being 0 to 4 and  $y$  being 1 to 4,  $A$  is the residue of an organic pigment containing  $x + y$  cyclic or open  $-NH-$  groups, and the  $H$  as well as  $CH_3$  in formula I and II are bound to the above mentioned  $N$ .

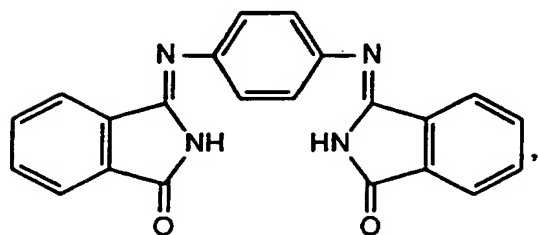
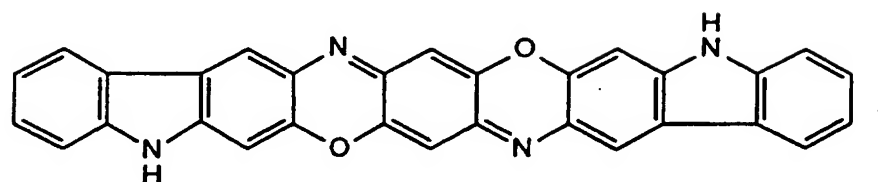
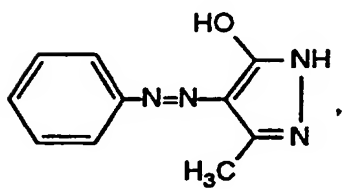
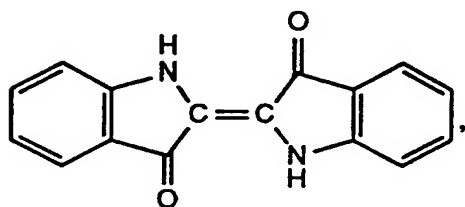
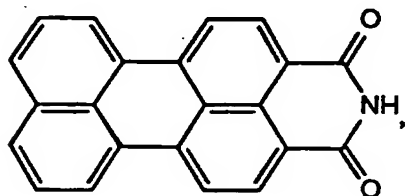
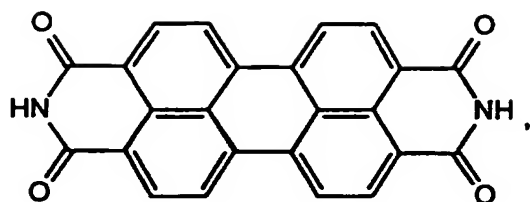
$x + y$  is preferably 1 or 2.

$A$  in formulae I and II is preferably the residue of a pigment selected from the group consisting of the quinacridone, anthraquinone, perylene, indigo, quinophthalone, isoindolinone, isoindoline, dioxazine, diketopyrrolopyrrole, phthalocyanine or azo series.

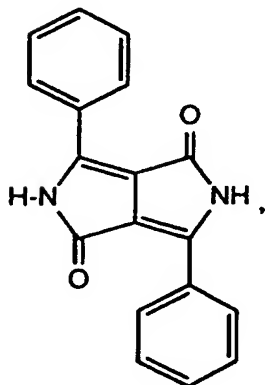
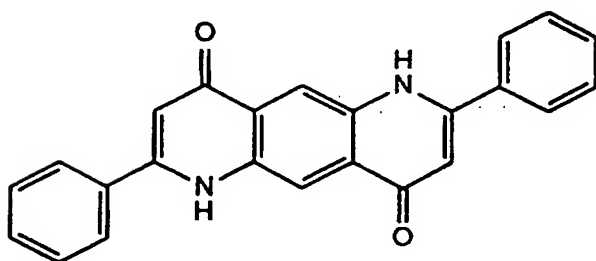
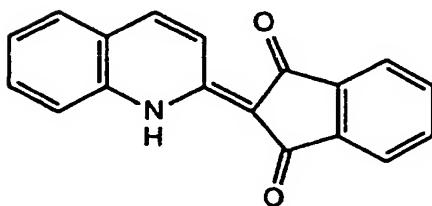
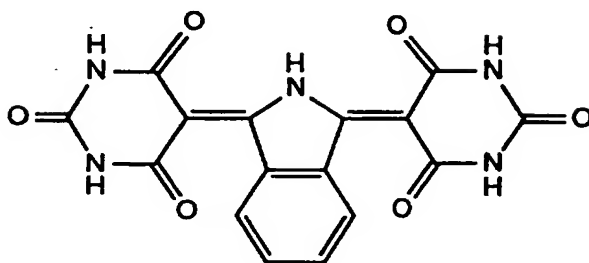
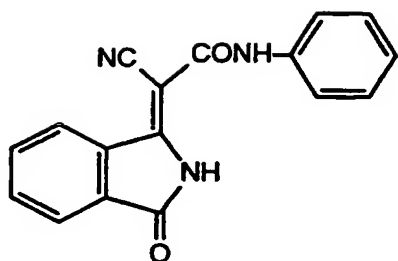
Examples of such organic pigments include:



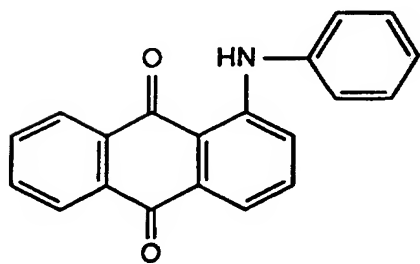
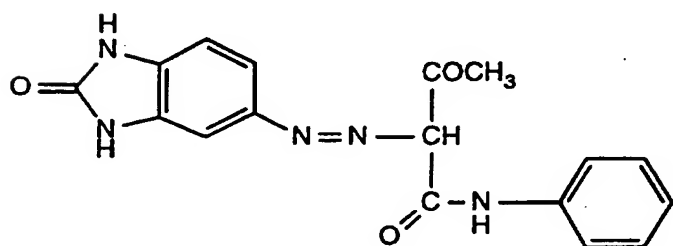
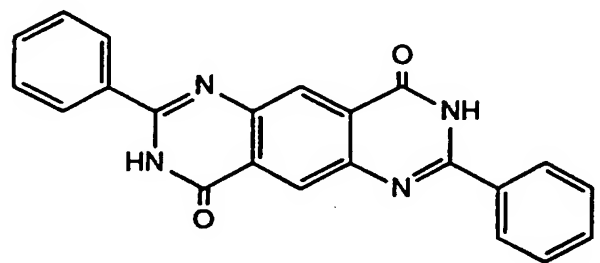
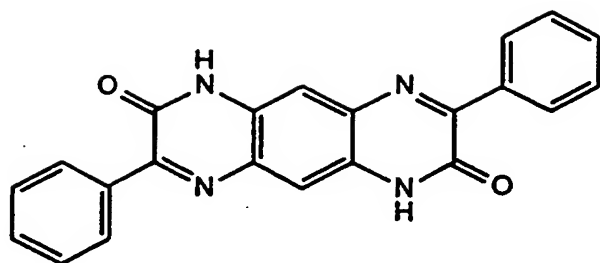
- 3 -



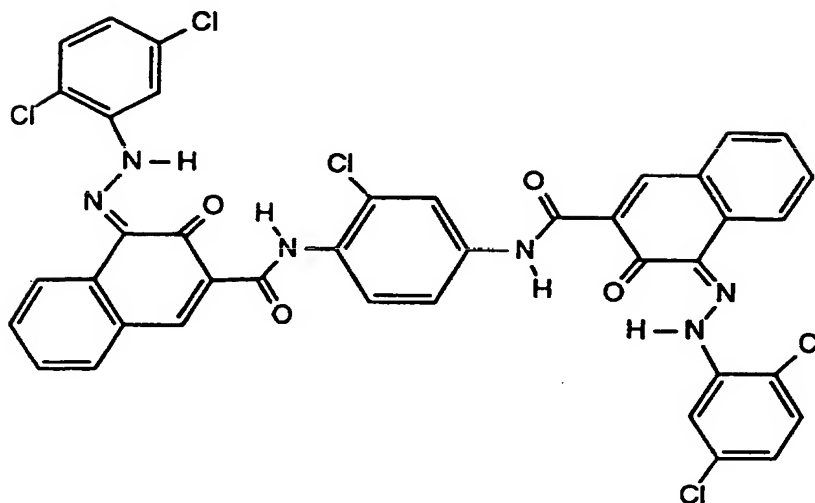
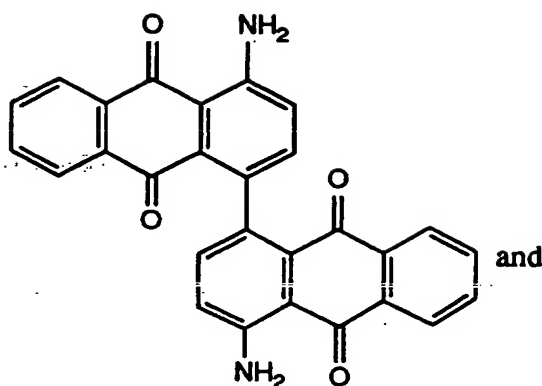
- 4 -



- 5 -



- 6 -



as well as all the known derivatives of the above chromophores.

The bases eligible for use in the process of the instant invention are, for example, the alkaline metals themselves, such as lithium, sodium or potassium as well as their hydroxides and carbonates, or alkaline metal amides, such as lithium, sodium or potassium amide or alkaline metal hydrides, such as lithium, sodium or potassium hydride, or alkaline earth or alkaline metal alcoholates, which are derived especially from primary, secondary or tertiary aliphatic alcohols with 1 to 10 C-atoms, e.g., lithium, sodium or potassium methylate, ethylate, n-propylate, isopropylate, n-butylate, sec.-butylate, tert.-butylate, 2-methyl-2-butylate, 2-methyl-2-pentylate, 3-methyl-3-pentylate, 3-ethyl-3-pentylate, and further, preferably, organic aliphatic, aromatic or heterocyclic N-bases, especially, for example, diazabicyclooctene, diazabicycloundecene, trialkylamines, such as trimethyl- or triethylamine, pyridine and substituted pyridines, such as 4-dimethylaminopyridine. The above bases can be used also as mixtures.



- 7 -

Especially preferred bases are, for example, organic aliphatic, aromatic or heterocyclic N-bases, particularly, trimethylamine, triethylamine, pyridine and 4-dimethylaminopyridine.

In the instant invention, the reaction can be accomplished with or without using a solvent. When solvents are to be used, polar organic solvents are preferred. Examples of such solvents are ethers, such as tetrahydrofuran or dioxane, or glycol ethers, such as ethylene glycol methyl ether, ethylene glycol ethylether, acetonitrile, benzonitrile, N,N-dimethylformamide, N,N-dimethylacetamide, nitrobenzene, N-methylpyrrolidone, halogenated aliphatic or aromatic hydrocarbons, such as trichloroethane, benzene or benzene substituted by alkyl, alkoxy or halogen, e.g., toluene, xylene, anisole or chlorobenzene, or aromatic N-heterocycles, such as pyridine, picoline or quinoline. These solvents can be used also as mixtures.

Especially preferred solvents are, for example, tetrahydrofuran, N,N-dimethylformamide, dioxane, dimethylsulfoxide, N,N-dimethylacetamide or N-methylpyrrolidone.

The reaction of the instant invention is carried out by simply mixing the compound represented by formula II, dimethylcarbonate and a base, with or without a solvent, and stirring the thus prepared mixture.

When no solvent is used, the compound of formula II, the base and dimethylcarbonate are mixed in a molar ratio of 1 : 0.1-1000 : 1-100000, preferably 1 : 1-100 : 10-10000, more preferably 1 : 1-50 : 10-1000 and most preferably 1 : 1-10 : 10-500. In this case, the dimethylcarbonate acts as a N-methylating agent as well as a reaction solvent. If a solvent is to be used, the compound of formula II, the base and dimethylcarbonate are added to the solvent such that their molar ratio is 1 : 0.1-100 : 0.1-100, preferably 1 : 1-50 : 1-50, more preferably 1 : 1-20 : 1-20 and most preferably 1 : 1-10 : 1-10. The solvent is used such that the concentration of the compound of formula II is 0.00001-100 mol/l, preferably 0.001-10 mol/l, more preferably 0.01-1 mol/l and most preferably 0.05-0.5 mol/l.

The reaction is carried out in air or in an inert atmosphere. Preferably, it is accomplished in an inert atmosphere such as for example under nitrogen gas, argon or helium. A nitrogen atmosphere is especially preferred.

- 8 -

The pressure under which the reaction is carried out may be varied within the range of from ambient pressure to a high pressure e.g. 500 atm. But, from the viewpoint of ease in operation, ambient pressure is especially preferred.

The reaction temperature is preferably 30-250°C, more preferably 50-200°C and most preferred 80-150°C.

The reaction is accomplished preferably for 1-100 hours, more preferably 2-80 hours and most preferably 2-50 hours.

The resulting compound of formula I is usually a mixture of compounds with a different degree of N-methylation. The longer the reaction time, the higher the yield in compounds of formula I with higher degree of N-methylation if  $x + y$  is equal to or larger than 2. Therefore, if it is desired to separate the components with different degree of N-methylation, the reaction mixture after reaction is subjected to a separation process. Any conventional separation method, such as one in which the difference in solubility in a solvent is used or a one in which a separating column is used, can be applied for this purpose. However, the separation using a column is especially preferred. Most preferably, the reaction product is separated by silica gel column chromatography using a non-polar or polar organic solvent e.g. hexane, dichloromethane or ethyl acetate. Suitable conditions for silica gel column chromatography are well known in the art.

In the process according to the instant invention, the compound represented by formula I is obtained in a yield of up to 92 %.

As described above, the present process makes it possible to prepare N-methylated organic pigments easily and at a high production yield without using toxic and expensive compounds such as methyl iodide or dimethyl sulfate. Therefore, the process of the invention is environmentally very safe and economical.

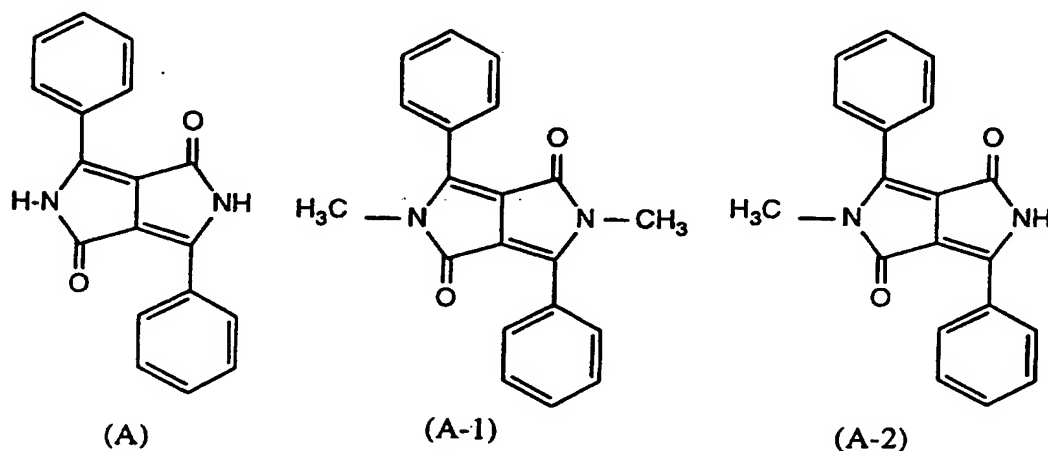
### Examples

#### Example 1

A solution of 0.7 g (6.92 mmol) of triethylamine in 5 ml of dimethyl acetamide (hereinafter, referred to as DMA) is added to a suspension of 0.5 g (1.73 mmol) of 1,4-diketo-pyrrolo[3,4-c]-pyrrole as indicated by A below in 25 ml of DMA, to which

- 9 -

0.374 g (4.15 mmol) of dimethyl carbonate are further added. The suspension is heated to 110°C and stirred for 48 hours at said temperature under N<sub>2</sub> atmosphere. The reaction system is then mixed with 100 ml water, and the mixture is subjected to extraction using dichloromethane. The organic phase is washed with water, dried over magnesium sulfate and subsequently concentrated under vacuum. The residue (0.49 g) is chromatographed on a silica gel column using a solvent mixture consisting of 83 vol% dichloromethane and 17 vol% ethyl acetate. The first yellow-orange zone yields 315 mg of a compound A-1, and the second orange-yellow zone yields 151 mg of a compound A-2. NMR, mass spectroscopic and elementary analyses reveal that these compounds A-1 and A-2 are respectively N,N'-dimethyl-1,4-diketo-pyrrolo[3,4-c]-pyrrole as indicated by A-1 and N-methyl-1,4-diketo-pyrrolo[3,4-c]-pyrrole as indicated by A-2. The yield of A-1 is 46 %, while that of A-2 is 23 %.



#### Analytical data:

##### For A-1:

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.89 (m, 4H, Ar-H), 7.54 (m, 6H, Ar-H), 3.34 (s, 6H, N-CH<sub>3</sub>).

Mass spectrometry (*m/e*): 316 (M<sup>+</sup>, 100 %).

Elemental analysis (%): C, 75.94; H, 5.06; N, 8.86 (calculated) and C, 75.88; H, 5.22; N, 8.78 (observed).

##### For A-2:

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.05 (s, br, 1H, N-H), 8.31 (m, 2H, Ar-H), 7.92 (m, 2H, Ar-H), 7.54

- 10 -

(m, 6H, Ar-H), 3.41 (s, 3H, N-CH<sub>3</sub>).

Mass spectrometry (*m/e*): 302 (M<sup>+</sup>, 100 %).

Elemental analysis (%): C, 75.49; H, 4.63; N, 9.27 (calculated) and C, 75.43; H, 5.83; N, 9.09 (found).

### Example 2

2.9 ml (20.82 mmol) of triethylamine are added to a suspension of 0.5 g (1.73 mmol) of 1,4-diketo-pyrrolo[3,4-c]-pyrrole in 30 ml of dimethyl carbonate, which mixture is heated under reflux condition for 96 hours in a nitrogenic atmosphere. The resulting red-brown solution is concentrated under vacuum, and the residue is suspended in ethanol. The precipitate thereby formed is filtered and dried. NMR, mass spectroscopic and elemental analyses reveal that the red-brown crystalline product is N,N'-dimethyl-1,4-diketo-pyrrolo[3,4-c]-pyrrole. The yield is 0.25 g, which corresponds to 45.7 % in yield.

### Analytical data:

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.89 (m, 4H, Ar-H), 7.54 (m, 6H, Ar-H), 3.34 (s, 6H, N-CH<sub>3</sub>).

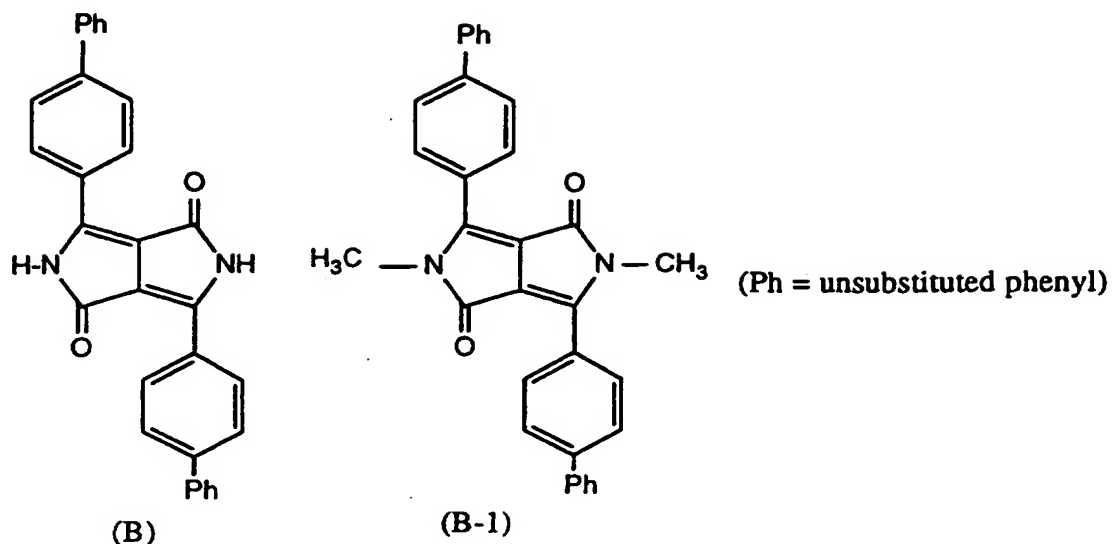
Mass spectrometry (*m/e*): 316 (M<sup>+</sup>, 100 %).

Elemental analysis (%): C, 75.94; H, 5.06; N, 8.86 (calculated) and C, 75.88; H, 5.36; N, 8.62 (observed).

### Example 3

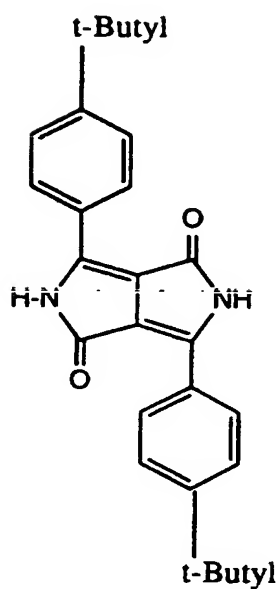
Reaction and separation are carried out similarly to Example 1 except that p-diphenyl-1,4-diketo-pyrrolo[3,4-c]-pyrrole (indicated by B below) is used instead of 1,4-diketo-pyrrolo[3,4-c]-pyrrole, reaction time is prolonged to 72 hours and a solvent mixture consisting of 98 vol% dichloromethane and 2 vol% ethyl acetate is used for the column separation. Analyses reveal that N,N'-dimethyl-p-diphenyl-1,4-diketo-pyrrolo[3,4-c]-pyrrole as indicated by B-1 is obtained in a yield of 13 %.

- 11 -

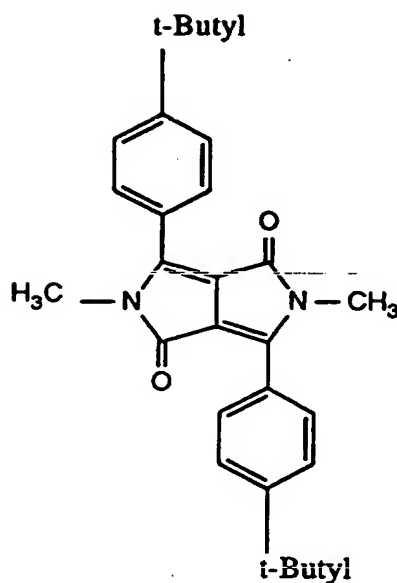
**Example 4**

Reaction and separation are carried out similarly to Example 1 except that di-p-tert-butyl-1,4-diketo-pyrrolo[3,4-c]-pyrrole (indicated by C below) is used instead of 1,4-diketo-pyrrolo[3,4-c]-pyrrole and a solvent mixture consisting of 50 vol% dichloromethane and 50 vol% ethyl acetate is used for the column separation. Analyses reveal that N,N'-dimethyl-di-p-tert-butyl-1,4-diketo-pyrrolo[3,4-c]-pyrrole (indicated by C-1) and N-methyl-di-p-tert-butyl-1,4-diketo-pyrrolo[3,4-c]-pyrrole (indicated by C-2) are obtained in yields of 76 % and 6.5 %, respectively.

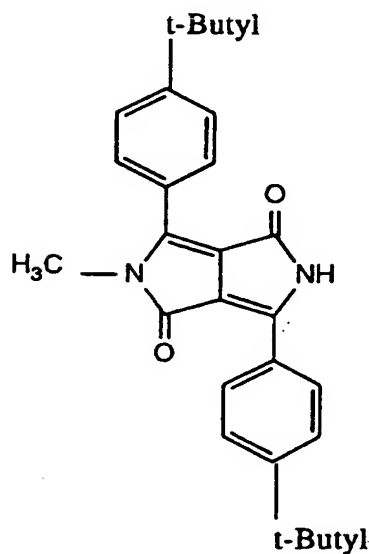
- 12 -



(C)



(C-1)



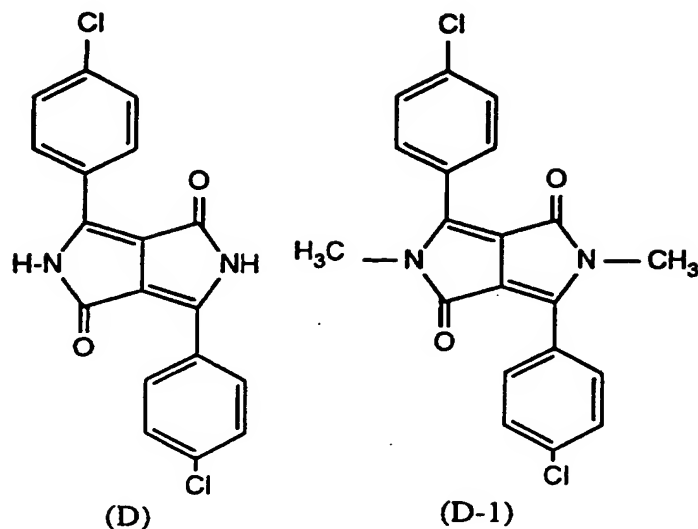
(C-2)

**Example 5**

Reaction and separation are carried out similarly to Example 1 except that di-p-chloro-1,4-diketo-pyrrolo[3,4-c]-pyrrole (indicated by D below) is used instead of 1,4-diketo-pyrrolo[3,4-c]-pyrrole and a solvent mixture consisting of 50 % dichloromethane and 50 % ethyl acetate is used for the column separation. Analyses reveal that N,N'-dimethyl-di-p-chloro-1,4-diketo-pyrrolo[3,4-c]-pyrrole (indicated by D-1

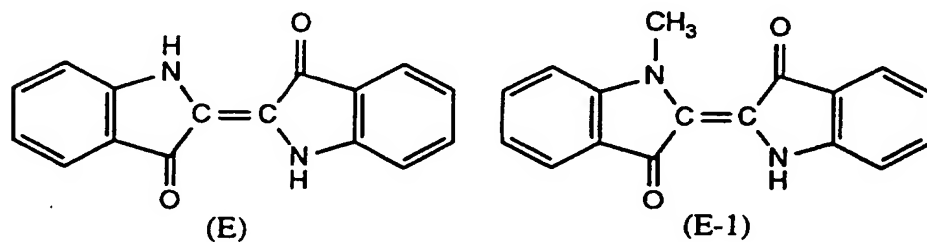
- 13 -

below) is obtained in a yield of 16 %.



#### Example 6

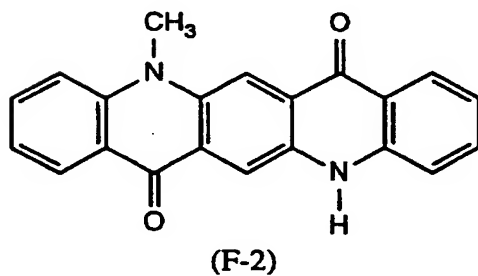
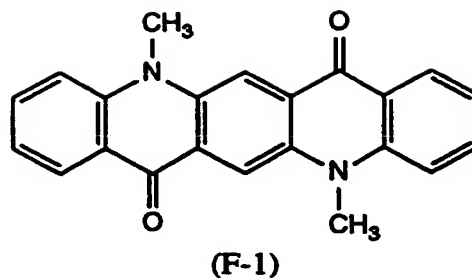
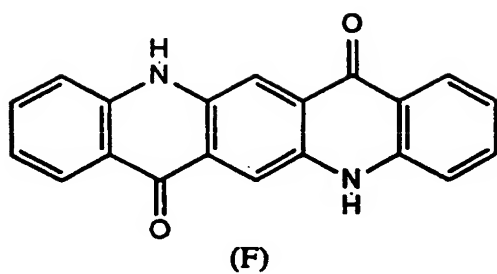
Reaction and separation are carried out similarly to Example 1 except that indigo as indicated by E below is used instead of 1,4-diketo-pyrrolo[3,4-c]-pyrrole, the reaction time is prolonged to 72 hours and dichloromethane is used for the column separation. Analyses reveal that N-methyl-indigo as indicated by E-1 is obtained in a yield of 7 %.



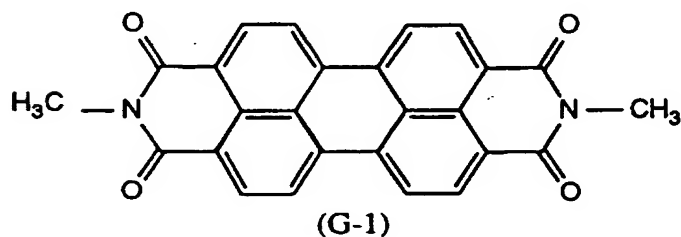
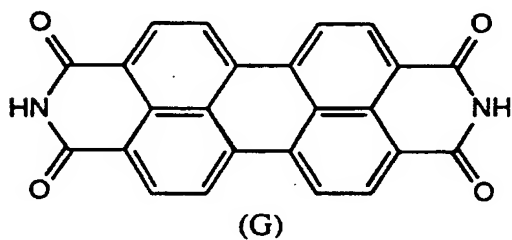
#### Example 7

Reaction and separation are carried out similarly to Example 1 except that quinacridone as indicated by F below is used instead of 1,4-diketo-pyrrolo[3,4-c]-pyrrole and the reaction time is prolonged to 72 hours. Analyses reveal that N,N'-dimethyl-quinacridone (indicated by F-1) and N-methyl-quinacridone (indicated by F-2) are obtained respectively in yields of 54 % and 42 %.

- 14 -

**Example 8**

Reaction and separation are carried out similarly to Example 1 except that perylenediimide as indicated by G below is used instead of 1,4-diketo-pyrrolo[3,4-c]pyrrole and the reaction time is prolonged to 96 hours. Analyses reveal that N,N'-dimethyl-perylenediimide (indicated by G-1) is obtained in a yield of 62 %.

**Example 9**

Reaction and purification are carried out similarly to Example 2 except that quinacridone is used instead of 1,4-diketo-pyrrolo[3,4-c]-pyrrole and the reaction time is shortened to



- 15 -

72 hours. N,N'-dimethyl-quinacridone is obtained in a yield of 92 %.

**Example 10**

Reeaction and purification are carried out similarly to Example 2 except that perylenediimide is used instead of 1,4-diketo-pyrrolo[3,4-c]-pyrrole.

N,N'-dimethyl-perylenediimide is obtained in a yield of 82 %.

- 16 -

What is claimed is:

1. A process for producing an organic pigment represented by general formula



characterized in that an organic pigment represented by formula



is reacted with dimethylcarbonate in the presence of a base with or without a solvent, wherein in formulae I and II  $x + y$  is an integer 1 to 4 with  $x$  being 0 to 4 and  $y$  being 1 to 4,  $A$  is the residue of an organic pigment containing  $x + y$  cyclic or open  $-NH-$  groups, and the  $H$  as well as  $CH_3$  in formula I and II are bound to the above mentioned  $N$ .

2. A process according to claim 1, wherein  $x + y$  is 1 or 2.
3. A process according to claim 1, wherein  $A$  in formulae I and II is preferably the residue of a pigment selected from the group consisting of the quinacridone, anthraquinone, perylene, indigo, quinophthalone, isoindolinone, isoindoline, dioxazine, diketopyrrolopyrrole, phthalocyanine or azo-series.
4. A process according to claim 1, wherein the base is one selected from the group consisting of alkaline metals, alkaline metal hydroxides, alkaline metal carbonates, alkaline metal amides, alkaline metal hydrides, alkaline earth metal or alkaline metal alcoholates, which are derived especially from primary, secondary or tertiary aliphatic alcohols with 1 to 10 C-atoms, and organic aliphatic, aromatic or heterocyclic N-bases, or a mixture of at least two thereof.
5. A process according to claim 1, wherein the base is selected from the group consisting of organic aliphatic, aromatic or heterocyclic N-bases, or a mixture of at least two thereof.
6. A process according to claim 1, wherein the base is trimethylamine, triethylamine, pyridine or 4-dimethylaminopyridine, or a mixture of at least two thereof.
7. A process according to claim 1, wherein the reaction is carried out in a solvent.

- 17 -

8. A process according to claim 7, wherein the solvent is a polar organic solvent or a mixture of at least two polar organic solvents.
9. A process according to claim 7, wherein the solvent is tetrahydrofuran, N,N-dimethylformamide, dioxane, dimethylsulfoxide, N,N-dimethylacetamide or N-methylpyrrolidone, or a mixture of at least two thereof.
10. A process according to claim 1, wherein the compound of formula II, the base and dimethylcarbonate are reacted in a molar ratio of 1 : 0.1-1000 : 1-100000, preferably 1 : 1-100 : 10-10000, more preferably 1 : 1-50 : 10-1000 and most preferably 1 : 1-10 : 10-500 for the case where no solvent is used.
11. A process according to claim 1, wherein the compound of formula II, the base and dimethylcarbonate are used in a molar ratio of molar ratio is 1 : 0.1-100 : 0.1-100, preferably 1 : 1-50 : 1-50, more preferably 1 : 1-20 : 1-20 and most preferably 1 : 1-10 : 1-10, and the solvent is used such that the concentration of the compound of formula II is 0.00001-100 mol/l, preferably 0.001-10 mol/l, more preferably 0.01-1 mol/l and most preferably 0.05-0.5 mol/l.
12. A process according to claim 1, wherein the reaction is carried out in an inert atmosphere.
13. A process according to claim 1, wherein the reaction is carried out at a temperature of preferably 30-250°C, more preferably 50-200°C and most preferred 80-150°C.

# INTERNATIONAL SEARCH REPORT

In: tional Application No  
PCT/EP 95/03462

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C09B67/20

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 027 743 (CHEMETRON CORPORATION) 2 October 1970 see claims; examples & US,A,3 673 192 cited in the application ---	1
A	EP,A,0 133 156 (CIBA-GEIGY AG) 13 February 1985 see page 10, line 11 - line 13; examples 1A,2,4-6 ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 18 no. 313 (C-1212) [6653] ,15 June 1994 & JP,A,06 065510 (NIPPON KAYAKU CO. LTD.) 8 March 1994, see abstract --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

2 January 1996

Date of mailing of the international search report

26.01.1996

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Ketterer, M

## INTERNATIONAL SEARCH REPORT

Int. onal Application No  
PCT/EP 95/03462

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 368 750 (SUMITOMO CHEMICAL COMPANY LTD. & DAIEI CHEMICAL COMPANY LTD.) 16 May 1990 see page 4, line 55 - page 5, line 5 ----	1
A	SYNTHESIS, no. 5, May 1986 STUTTGART DE, pages 382-383, M. LISSEL ET. AL. 'Dimethylcarbonat als Methylierungsmittel unter phasentransfer-katalytischen Bedingungen' cited in the application see page 382, column 2, line 14 - page 383, column 1 ----	1
A	FR,A,2 348 910 (BASF AG) 18 November 1977 see the whole document ----	1
A	EP,A,0 319 854 (BOEHRINGER INGELHEIM KG) 14 June 1989 see examples ----	1
A	JUSTUS LIEBIGS ANNALEN DER CHEMIE, no. 1, January 1987 WEINHEIM DE, pages 77-79, M. LISSEL 'N-Methylierung von Imidazol und Derivaten.' see the whole document ----	1
A	JOURNAL OF ORGANIC CHEMISTRY OF THE USSR (ZHURNAL ORGANICHESKOI KHIMII), vol. 20, no. 9 (2), September 1984 - 20 February 1985 NEW YORK US, pages 1771-1775, L.L. PUSHKINA ET. AL. 'Methylation of linear trans-quinacridone in a two-phase catalytic system.' cited in the application see page 1772; table 2 -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/EP 95/03462

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-2027743	02-10-70	CH-A- 536343 DE-A- 1963728 GB-A- 1279879 US-A- 3673192	30-04-73 10-09-70 28-06-72 27-06-72
EP-A-133156	13-02-85	CA-A- 1230341 JP-C- 1758542 JP-B- 4042431 JP-A- 60035056 US-A- 4585878 US-A- 4666455	15-12-87 20-05-93 13-07-92 22-02-85 29-04-86 19-05-87
EP-A-368750	16-05-90	DE-D- 68919047 DE-T- 68919047 JP-A- 2225569 US-A- 5017713	01-12-94 02-03-95 07-09-90 21-05-91
FR-A-2348910	18-11-77	DE-A- 2618033 BE-A- 853859 GB-A- 1573651 JP-A- 52131534 US-A- 4423247	10-11-77 24-10-77 28-08-80 04-11-77 27-12-83
EP-A-319854	14-06-89	DE-A- 3741883 DE-D- 3888113 FI-B- 89485 JP-A- 1190686 JP-B- 6045620	22-06-89 07-04-94 30-06-93 31-07-89 15-06-94